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# Pyrolysis–gas chromatography–mass spectrometry of poly(dialkylsilylenes)

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## Abstract

A series of silylene copolymers with di-*n*-alkyl substituent groups varying from dimethyl to di-*n*-hexyl were pyrolysed in an analytical pyrolyser coupled to a capillary GC–MS system. The thermal decomposition of the silylene copolymers begins at about 200°C and proceeds via cyclic oligomer formation. The pyrolysis at 300°C of those copolymers which contain dimethylsilylene units lead to tetracycles and pentacycles, but those which have ethyl or longer alkyl substituents decompose exclusively to tetracycles. The copolymer composition and structure were evaluated from the pyrolysis product distribution data. Mass spectra and GC retention indices were obtained on several di-*n*-alkylsilylene cyclotetramers and cyclopentamers.

## 1. Introduction

On line pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) is successfully used for studying thermal decomposition processes in polymers [1,2]. Pyrolysis of macromolecular chains leads mostly to gaseous and volatile products, their nature and amount being related to the chemical structure of the polymer and the pyrolysis temperature. The pyrolysis mechanism is often found to be analogous for polymers of the same type [3]. Relatively mild pyrolysis, around the temperature at which decomposition begins, yields oligomeric volatile species or relatively large fragments in many instances. The large thermal fragments usually preserve the original chemical structure of the macromolecule, hence information on the mon-

omer sequences of copolymers could also be obtained using these coupled techniques [4].

The thermal decomposition mechanism of poly(dimethyl-, poly(methylalkyl- and poly(methylphenylsilylenes) has been described previously [5]. Cyclic tetramer and pentamer formation proved to be the initial thermal decomposition mechanism for poly(methylalkylsilylenes) at 300–400°C.

The aim of this work was to relate the pyrolysis mechanism of poly(di-*n*-alkylsilylenes) with that of poly(dimethyl- and poly(methylalkylsilylenes) and to characterize the monomer distribution in a series of copolymers synthesized from two different di-*n*-alkylsilylene monomers. For these purposes qualitative and quantitative analysis of the initial thermal de-

composition products of a series of copolymers were performed.

## 2. Experimental

### 2.1. Materials

The copolymer samples were obtained from polymerization of a mixture of di-*n*-alkyldichlorosilanes in toluene with sodium under reflux, as described by Menescal and West [6].

### 2.2. Pyrolysis–GC–MS

Rapid pyrolyses were performed at 300°C for 10 s in a Chemical Data System Pyroprobe 120 equipped with a platinum coil and quartz sample tube interfaced either to a Hewlett-Packard Model 5880 A gas chromatograph with a flame ionization detector or to a Hewlett-Packard Model 5985 B gas chromatograph–mass spectrometer. The sample mass was about 100–200 µg. Helium carrier gas at a flow-rate of 20 ml/min purged the pyrolysis chamber held at 250°C; it was split in a ratio of 1:20 before being introduced into the fused-silica capillary column (25 m × 0.2 mm I.D.) coated with 0.33-µm dimethylsiloxane bonded phase (Hewlett-Packard U-1). A temperature programme was applied to the GC oven from 50 to 300°C at a rate of 6°C/min. The GC–MS interface was held at 300°C. The mass spectrometer was operated at 70 eV.

The temperature-programmed retention indices were determined using the *n*-alkane series of polyethylene (BDH, Poole, UK) pyrolysate together with dotriacontane and hexatriacontane standards (PolyScience, Evanston, IL, USA).

## 3. Results and discussion

Typical pyrolysis gas chromatograms (pyro-

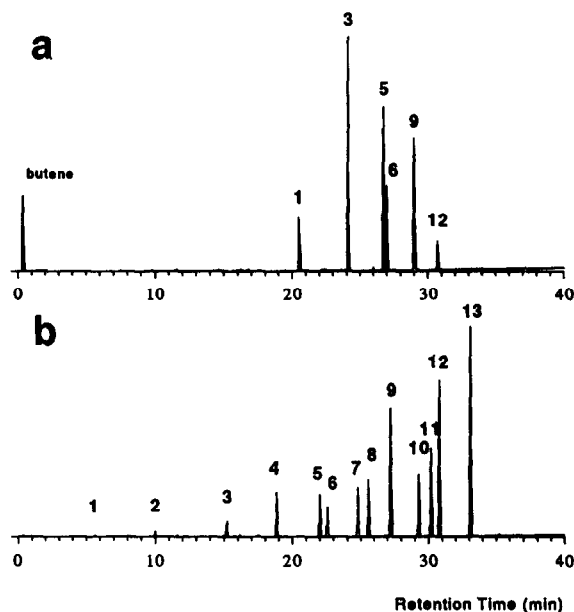


Fig. 1. Pyrograms obtained on a temperature-programmed U-1 capillary column. (a) Poly(diethylsilylene-co-di-*n*-butylsilylene); (b) poly(dimethylsilylene-co-di-*n*-butylsilylene). Peak numbers refer to the products in Table 1.

grams) are shown in Fig. 1. The pyrograms of copolymers containing dimethylsilylene units exhibited considerably more products than those of copolymers which contained only diethyl- or longer di-*n*-alkylsilylene units. The main peaks of the pyrograms proved to be oligocyclosilanes. The di-*n*-alkylsilylene copolymers which lack methyl groups decomposed exclusively to cyclotetramers, whereas copolymers containing dimethylsilylene monomers gave cyclopentamers in addition to cyclotetramers. The composition of these cyclooligomeric molecules corresponds to the possible combinations of the monomers. The pyrolysis products are listed in Table 1.

### 3.1. GC–MS analysis of the pyrolysis products

The identification of the pyrolysis products is based on their electron impact (EI) mass spectra, which exhibit abundant molecular ions. Typical spectra are shown in Figs. 2 and 3.

Table 1  
Pyrolysis products of copolymers  $(R_2Si)_n(R'_2Si)_m$

Peak No.	-cyclotetrasilane	-cyclopentasilane
1	Octa-R'-	
2		Decamethyl-
3	Hexa-R'-di-R-	
4		Octamethyl-di-R-
5	1,1,2,2-Tetra-R'-tetra-R-	
6	1,1,3,3-Tetra-R'-tetra-R-	
7		1,1,2,2-Tetra-R-hexamethyl-
8		1,1,3,3-Tetra-R-hexamethyl-
9	Di-R'-hexa-R-	
10		1,1,2,2-Tetramethylhexa-R-
11		1,1,3,3-Tetramethylhexa-R-
12	Octa-R-	
13		Dimethylocta-R-

R = *n*-Propyl, *n*-butyl, *n*-pentyl, *n*-hexyl; R' = methyl-, ethyl-, *n*-propyl, *n*-butyl, *n*-pentyl.

In the mass spectra of tetracycles even-mass number ions indicate 1-alkene elimination. The ions at  $m/z$  344, 288, 232 and 176 correspond to the elimination of one to four 1-butene molecules from a tetramethyltetra-*n*-butylcyclotetrasilane molecule in the spectra shown in Fig. 2. Fig. 2 also shows that the spectra of the isomers are very similar. However, the trimethylsilyl ion at  $m/z$  73 is less abundant from the isomer of longer retention time. Taking into consideration that trimethylsilyl ion most probably originates from tetramethyldisilyl dyad, peak 6 is assigned to 1,1,3,3-tetramethyl-2,2,4,4-tetra-*n*-butylcyclotetrasilane. This is in accordance with GC retention data, which predict a longer retention time for the isomer of more elongated shape [7]. The isomeric peaks 7–8 and 10–11 were assigned similarly.

In the mass spectra of cyclopentasilanes the abundant even-mass ions originate from the cleavage of the ring. The spectra of octamethyl-di-*n*-alkylcyclopentasilanes show abundant ions at  $m/z$  188 and 202 (Fig. 3), which are probably due to  $Si_4Me_5H$  and  $Si_4Me_6$  ions. A similar fragmentation may take place in hexamethyltetra-*n*-alkylcyclopentasilanes (Fig. 4) accompanied by 1-alkene elimination, resulting in  $Si_4Me_4RH$  ions at  $m/z$  230, 244 and 258 in the

spectra of these pentacycles with R = *n*-butyl, *n*-pentyl and *n*-hexyl, respectively.

### 3.2. GC retention indices of the pyrolysis products

Several quasi-homologous series can be distinguished among the oligocyclosilanes obtained by pyrolysis of the copolymers, in which the members differ in the length of the di-*n*-alkyl substituents. The temperature-programmed retention indices of the pyrolysis products of the copolymers measured on a methylsiloxane GC phase are listed in Table 2.

The molecules of homosubstituted cyclotetrasilanes form a series in which the length of all eight alkyl substituents are varied alike from methyl to *n*-hexyl; therefore, a regular change in their retention indices is expected as a function of their molecular mass. However, from the plot of these data in Fig. 5, an irregularity is observed regarding the points for methyl- and ethyl-substituted cyclotetrasilanes, indicating that some retention-determinating factor (ring conformation [8] or coverage of the silicon atoms by the substituents) is different for these molecules. Octamethylcyclotetrasilane has a lower and

Table 2  
Temperature programmed retention indices ( $I_{PT}$ ) of cyclooligosilanes

Substituent	$I_{PT}$	Substituent	$I_{PT}$
<i>Cyclotetrasilanes</i>			
Octamethyl-	1229	Octaethyl-	2071
Octapropyl-	2341	Octabutyl-	2769
Octapentyl-	3222	Octahexyl-	3685
Hexamethyldibutyl-	1726	Hexaethyldipropyl-	2159
-pentyl-	1894	-butyl-	2292
-hexyl-	2073	-pentyl-	2452
		-hexyl-	2619
Hexapropyldibutyl-	2453	Hexabutyl-dipentyl-	2914
-pentyl-	2591	-hexyl-	3030
-hexyl-	2745	Hexapentyl-dihexyl-	3353
1,1,2,2-Tetramethyltetra-butyl-	2134	1,1,2,2-Tetraethyltetrapropyl-	2230
-pentyl-	2438	-butyl-	2473
-hexyl-	2759	-pentyl-	2758
		-hexyl-	3053
1,1,3,3-Tetramethyltetra-butyl-	2176	1,1,3,3-Tetraethyltetrapropyl-	2240
-pentyl-	2500	-butyl-	2496
-hexyl-	2832	-pentyl-	2795
		-hexyl-	3103
1,1,2,2-Tetrapropyltetra-butyl-	2577	1,1,2,2-Tetra-butyltetrapentyl	3021
-pentyl-	2828	-hexyl-	3263
-hexyl-	3105	-pentyltetrahexyl-	3461
1,1,3,3-Tetrapropyltetra-butyl-	2580	1,1,3,3-Tetra-butyltetrapentyl	3045
-pentyl-	2838	-hexyl-	3278
-hexyl-	3122	-pentyltetrahexyl-	3465
Dimethylhexabutyl-	2496	Diethylhexapropyl-	2294
-pentyl-	2918	-butyl-	2637
-hexyl-	3302	-pentyl-	3026
		-hexyl-	3415
Dipropylhexabutyl-	2671	Dibutylhexapentyl-	3148
-pentyl-	3036	-hexyl-	3481
-hexyl-	3450	Dipentylhexahexyl-	3565
<i>Cyclopentasilanes</i>			
Decamethyl-	1475	Octamethyldibutyl-	1954
Octamethyldipentyl-	2122	-hexyl-	2298
1,1,2,2,3,3-Hexamethyltetra-butyl-	2336	1,1,2,2,4,4-Hexamethyltetra-butyl-	2400
-pentyl-	2627	-pentyl-	2719
-hexyl-	2920	-hexyl-	3016
1,1,2,2-Tetramethylhexa-butyl-	2675	1,1,3,3-Tetramethylhexa-butyl-	2748
-pentyl-	3053	-pentyl-	3143
-hexyl-	3412	-hexyl-	3528
Dimethyloctabutyl-	2969	Dimethyloctapentyl-	3399
-hexyl-	3781		

octaethylcyclotetrasilane a higher retention index than expected from their molecular masses.

Figs. 6 and 7 show that the retention index

increment of a methylene group (*i.e.*, the slope of the lines connecting two neighbouring points) is lowered as the number of the longer sub-

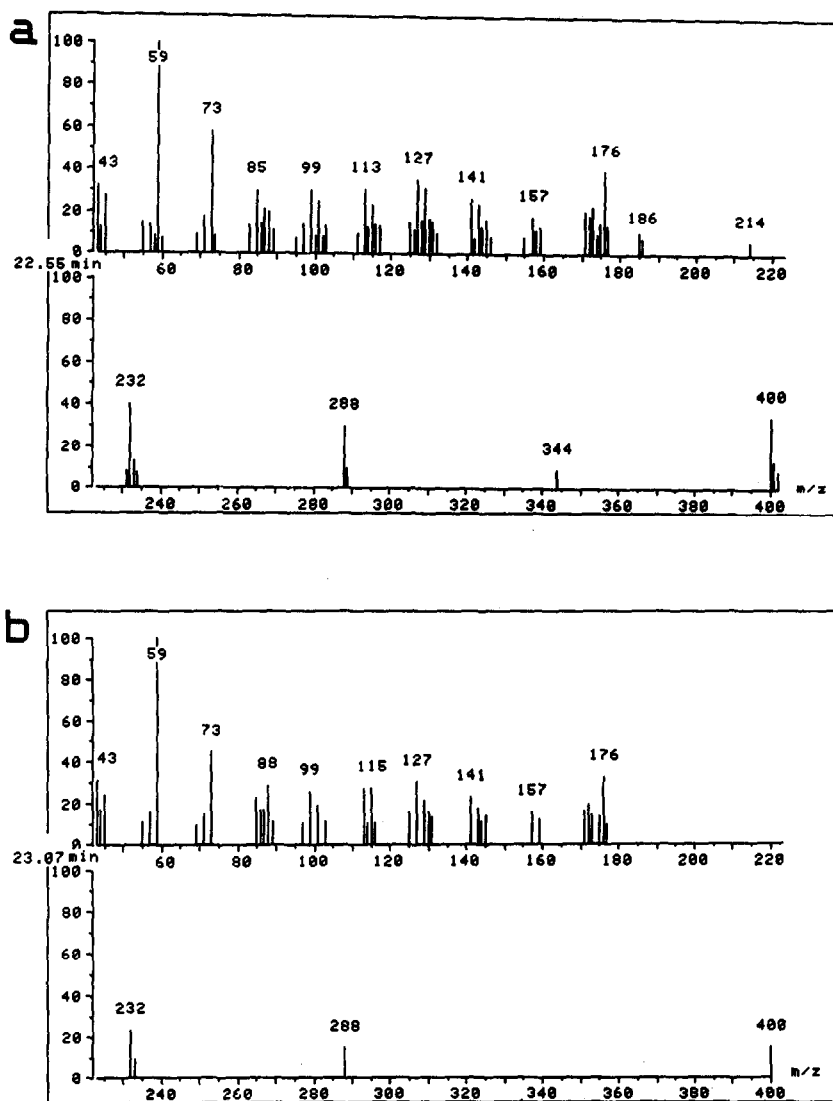


Fig. 2. Mass spectra of (a) 1,1,2,2-tetramethyl-3,3,4,4-tetra-*n*-butyl- and (b) 1,1,3,3-tetramethyl-2,2,4,4-tetra-*n*-butyl-cyclotetrasilane.

stituents or the substituent length is increased in the molecule of cyclotetrasilanes. Moreover, the retention indices of hexaethylcyclotetrasilanes are relatively higher than expected from the general trend of the other values. In Fig. 6 the points for the 1,1,2,2-tetramethyl isomers are connected with a full line and those for the 1,1,3,3-tetramethyl isomers with a dashed line among the points of tetramethyltetra-*n*-alkyl-cyclotetrasilanes.

### 3.3. Copolymer characterization by pyrolysis product distribution

The areas of the peaks detected by flame ionization detection (FID) were transformed into relative molar amounts using relative response factors [9]. The peak areas of the total ion GC-MS pyrograms may also be considered as an approximation for relative molar amounts. The quantitative data obtained by the two kinds

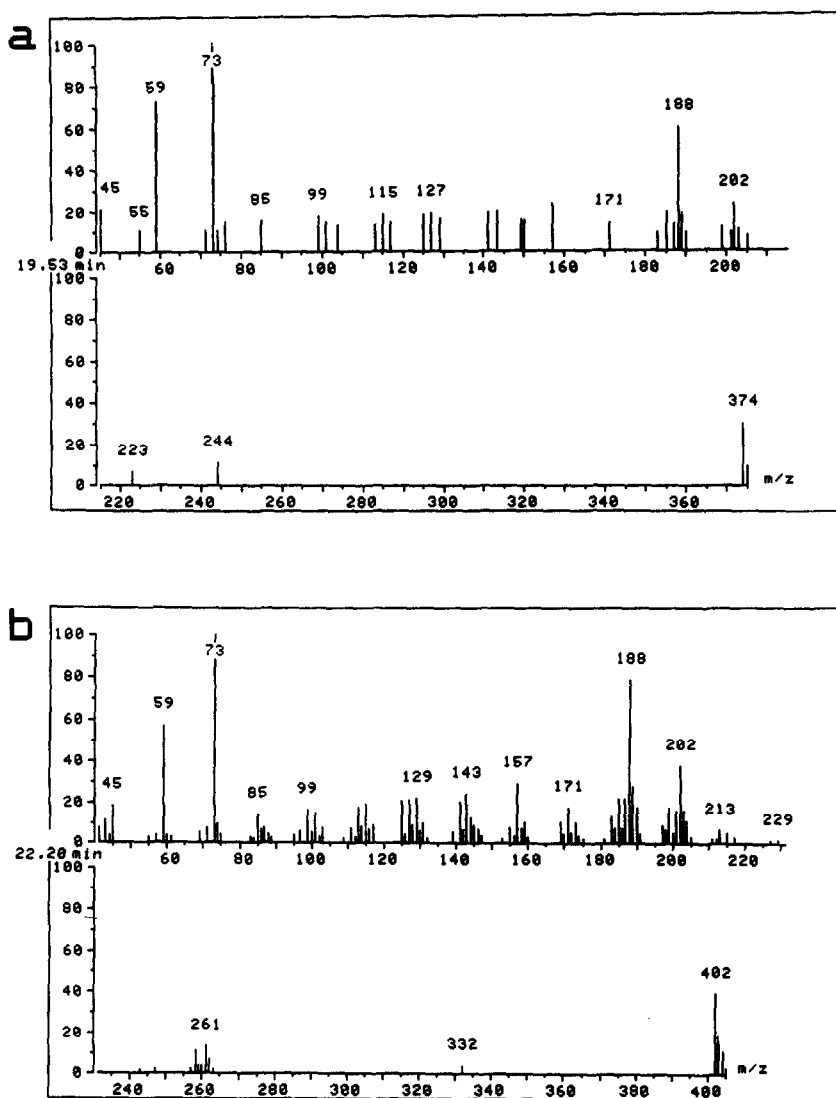


Fig. 3. Mass spectra of (a) octamethyldi-*n*-butyl- and (b) octamethyldi-*n*-pentylcyclopentasilane.

of detection are shown for di-*n*-propyl-diethylsilylene (sample 13) and di-*n*-pentyl-dimethylsilylene (sample 9) copolymers in Table 3. Product amounts were also calculated assuming a random monomer distribution in the copolymer and are given in Table 3 for comparison.

Summing separately the molar amounts of the different di-*n*-alkylsilylene units occurring in the different cyclosilanes, the ratio of the sums gives the copolymer composition. The molar ratios (*n*/*m* values) of the two monomers evaluated in

this way are given in Table 4. Table 4 shows a fairly good agreement with the copolymer compositions obtained from NMR spectra of copolymer solutions [6] for most of the samples. However, huge deviations occur for the di-*n*-hexylsilyl-containing copolymers, owing to the loss of part of the low-volatility products (having retention indices above 3300). The deviations could be decreased by increasing the temperature of the interface between the pyrolyser and the gas chromatograph.

A number characterization of the monomer

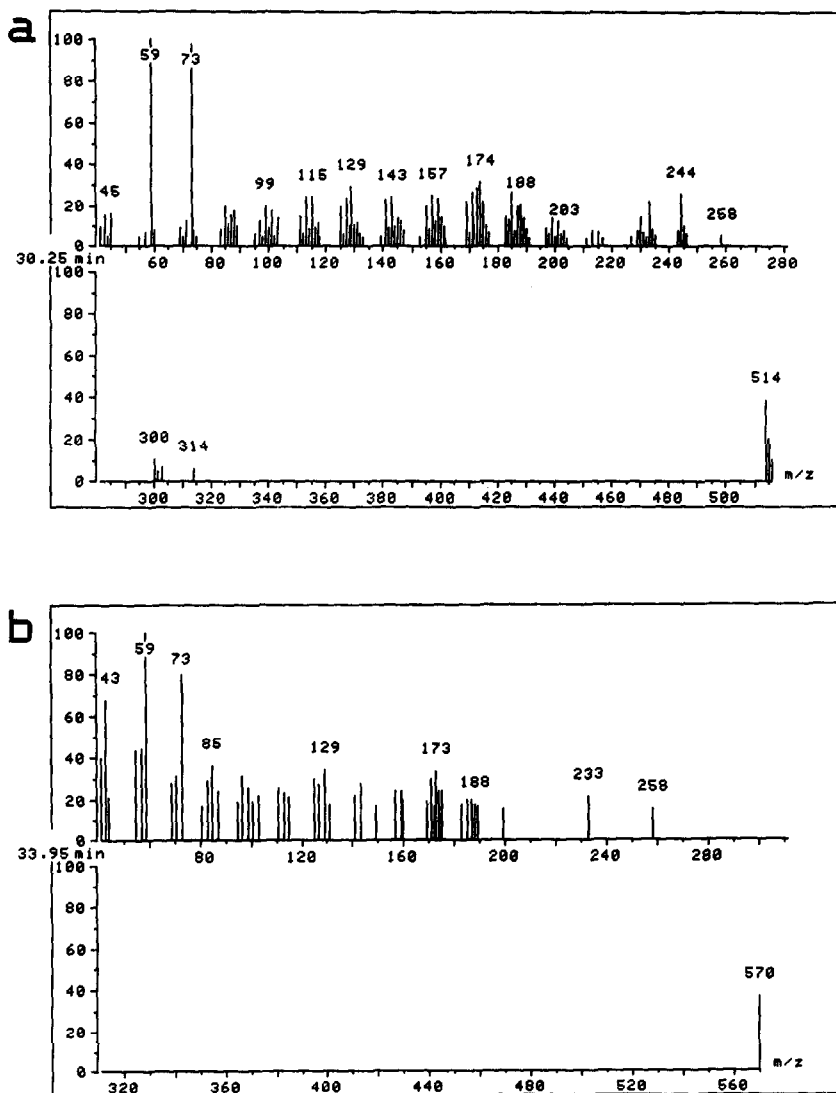


Fig. 4. Mass spectra of (a) hexamethyltetra-*n*-pentyl- and (b) hexamethyltetra-*n*-hexylcyclopentasilane.

distribution along the copolymer chain is available by counting the relative occurrence of the three possible disilylene dyads in the pyrolysate cyclosilanes. The relative occurrences of the three kinds of dyads are given in Table 5 together with the deviations to the values calculated for a random copolymer structure. According to these data, most of the samples investigated have random copolymer structures. Table 5 even demonstrates that reliable information

may be obtained on the copolymer structure by pyrolysis-GC also when part of the low-volatility pyrolysis products are lost.

#### 4. Conclusions

This Py-GC-MS investigation of di-*n*-alkylsilylene copolymers revealed that a thermal decomposition mechanism leading to cyclic

Table 3  
Pyrolysis product distribution of some copolymers  $(R_2Si)_n(R'_2Si)_m$

Sample No. <sup>a</sup>	Method <sup>b</sup>	Cyclotetramers (mol %)						Cyclopentamers (mol %)						
		1	3	5	6	9	12	2	4	7	8	10	11	13
9 (l)	FID	0.8	11.0	14.9	4.2	9.6	3.5	1.3	13.4	8.3	8.2	8.7	7.1	8.9
	MS	0.1	9.3	10.3	5.6	11.8	6.3	1.3	14.5	9.7	10.3	7.5	8.0	5.3
	Calc.	2.8	11.1	10.9	5.5	10.7	2.6	1.8	9.1	8.9	8.9	8.7	8.7	8.6
9 (h)	FID	0.4	9.1	20.2	5.1	18.2	10.4	0.8	5.1	4.1	4.5	6.7	7.8	7.6
	Calc.	2.0	11.1	15.1	7.6	20.7	6.9	0.5	3.4	4.6	4.6	6.3	6.3	8.6
13	FID	8.6	28.1	25.3	10.9	21.5	5.5	0	0	0	0	0	0	0
	MS	7.1	29.9	23.9	12.8	22.0	4.5	0	0	0	0	0	0	0
	Calc.	8.6	29.1	24.6	12.3	20.9	3.9							

<sup>a</sup> Sample numbers refer to those given in Table 4; (l) and (h) = low- and high-molecular-mass fraction, respectively.

<sup>b</sup> Source of quantitative evaluation: FID = flame ionization detection; MS = mass spectrometric total ion; calc. = calculated values for a random copolymer structure.

pentamers takes place only with polysilanes containing methyl substituents. According to the pyrolysis product distributions, the relative amount of pentamers to tetramers is considerably higher in the pyrolysate of the low-molecular-mass fraction of the investigated copolymer

samples (Table 3). These observations suggest that the pentacycle formation may be a backbiting process occurring from the terminus of the macromolecular chain. The results can be explained if the backbiting decomposition to pentacycles is prevented by the presence of longer

Table 4  
Composition of copolymers  $(R_2Si)_n(R'_2Si)_m$

Sample No. <sup>a</sup>	R	R'	$n/m^b$		
			Py	<sup>29</sup> Si NMR	<sup>1</sup> H NMR
1	<i>n</i> -Hexyl	<i>n</i> -Pentyl	0.39	–	–
2	<i>n</i> -Hexyl	<i>n</i> -Butyl	0.58	–	0.84
3	<i>n</i> -Hexyl	<i>n</i> -Propyl	0.66	0.75	–
4	<i>n</i> -Hexyl	Ethyl	0.60	1.16	1.11
5 (l)	<i>n</i> -Hexyl	Methyl	0.20	–	0.32
5 (h)			0.72	1.18	1.33
6	<i>n</i> -Pentyl	<i>n</i> -Butyl	0.82	–	0.89
7	<i>n</i> -Pentyl	<i>n</i> -Propyl	0.89	0.96	0.98
8	<i>n</i> -Pentyl	Ethyl	0.86	0.90	0.81
9 (l)	<i>n</i> -Pentyl	Methyl	0.98	–	0.89
9 (h)			1.36	–	1.30
10	<i>n</i> -Butyl	<i>n</i> -Propyl	1.46	1.50	1.45
11	<i>n</i> -Butyl	Ethyl	0.79	0.80	0.87
12 (l)	<i>n</i> -Butyl	Methyl	0.89	–	0.79
12 (h)			2.27	–	2.19
13	<i>n</i> -Propyl	Ethyl	0.87	0.83	0.79

<sup>a</sup> (l) = Low- and (h) = high-molecular-mass fraction.

<sup>b</sup> Py = Measured by pyrolysis; NMR = measured by NMR spectroscopy [6].



Table 5  
Relative occurrence of dyads in copolymers  $(R_2Si)_n(R'_2Si)_m$

Sample No. <sup>a</sup>	R	R'	Relative molar amounts <sup>b</sup>					
			$(R_2Si)_2$		$(R_2Si)(R'_2Si)$		$(R'_2Si)_2$	
1	<i>n</i> -Hexyl	<i>n</i> -Pentyl	51	0	41	+1	8	0
2	<i>n</i> -Hexyl	<i>n</i> -Butyl	41	+1	44	-3	15	+1
3	<i>n</i> -Hexyl	<i>n</i> -Propyl	38	+2	44	-4	18	+2
4	<i>n</i> -Hexyl	Ethyl	38	-1	49	+2	13	-1
5 (l)	<i>n</i> -Hexyl	Methyl	69	0	28	0	2	-1
5 (h)			33	-1	50	+1	17	-1
6	<i>n</i> -Pentyl	<i>n</i> -Butyl	32	+2	45	-4	22	+2
7	<i>n</i> -Pentyl	<i>n</i> -Propyl	28	0	50	0	22	0
8	<i>n</i> -Pentyl	Ethyl	30	+1	48	-2	22	+1
9 (l)	<i>n</i> -Pentyl	Methyl	24	-1	51	+1	26	0
9 (h)			18	0	49	0	33	0
10	<i>n</i> -Butyl	<i>n</i> -Propyl	17	0	48	0	35	0
11	<i>n</i> -Butyl	Ethyl	32	+1	48	-1	20	+1
12 (l)	<i>n</i> -Butyl	Methyl	26	-2	54	+4	26	-2
12 (h)			8	-1	45	+2	47	-1
13	<i>n</i> -Propyl	Ethyl	28	-1	51	+1	21	-1

<sup>a</sup> (l) = Low- and (h) = high-molecular-mass fraction.

<sup>b</sup> Values in the second columns are deviations of found values from values calculated for a random copolymer structure.

*n*-alkyl groups on the silicon atoms. Some other mechanism, as yet not clear, must then be invoked to explain the formation of tetracycles at higher temperature.

The qualitative and quantitative analysis of the volatile products applying pyrolysis–GC–MS re-

sulted in useful information about the copolymer composition and structure. In addition, GC retention data revealed differences between the retention index increments of methyl, ethyl and longer *n*-alkyl substituents of cyclotetra- and cyclopentasilanes.

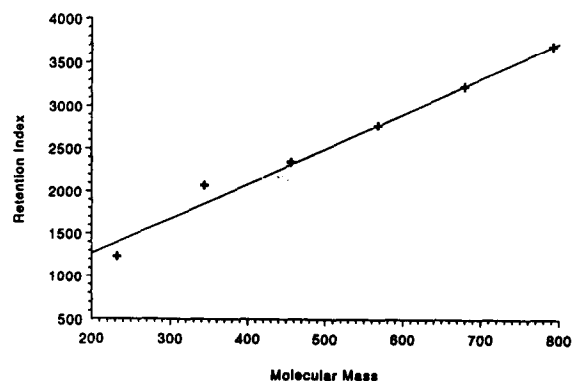


Fig. 5. Temperature-programmed retention indices of octamethyl-, -ethyl-, -*n*-propyl-, -*n*-butyl-, -*n*-pentyl- and -*n*-hexylcyclotetrasilane plotted against their molecular masses.

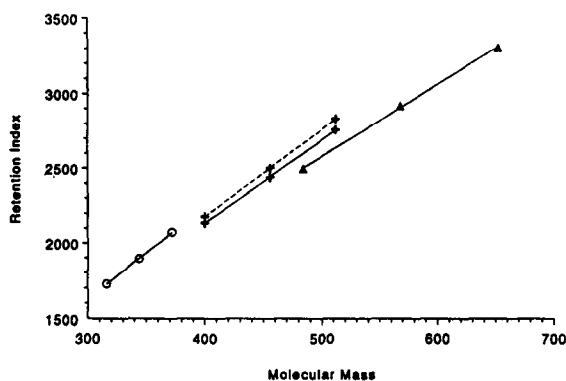


Fig. 6. Temperature-programmed retention indices of (○) hexamethyldi-, (+) tetramethyltetra- and (▲) dimethylhexa-*n*-butyl-, -*n*-pentyl- and -*n*-hexylcyclotetrasilane.

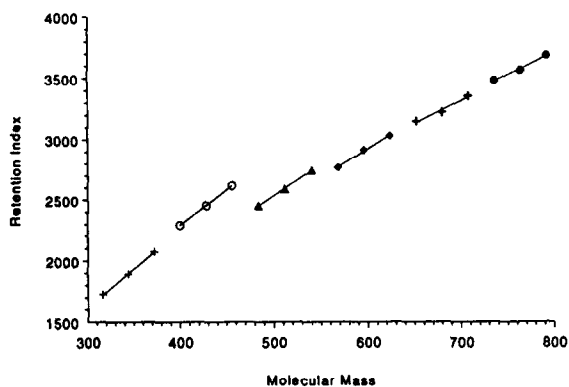


Fig. 7. Temperature-programmed retention indices of (+) hexamethyl-, (O) hexaethyl-, ( $\Delta$ ) hexa-*n*-propyl-, ( $\blacklozenge$ ) hexa-*n*-butyl-, (+) hexa-*n*-pentyl- and (O) hexa-*n*-hexyl-di-*n*-butyl-, -di-*n*-pentyl- and -di-*n*-hexylcyclotetrasilane.

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